PB-237 804-T

POLLUTION OF THE SEA BY PETROLEUM

Juan Albaiges Riera

Environmental Protection Agency
Research Triangle Park, North Carolina

1974

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

312074

NTIS

PB 237 804 -T

EPA-TR 63-75

Juan Albaiges Riera

POLLUTION OF THE SEA BY PETROLEUM

[La contaminacion del mar por el petroleo]

oilgas, No. 75, March, 1974, pp. 5-14

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
U S Department of Commerce
Springfield VA 22151

Translated for the
ENVIRONMENTAL PROTECTION AGENCY
by
Translation Consultants, Ltd., Arlington, Virginia

Juan Albaiges Riera *

POLLUTION OF THE SEA BY PETROLEUM

(The author is a scientific researcher at the Barcelona Organic Chemistry Institute. He has been with the institute since 1971. His doctorate in science is from the University of Barcelona. He is a graduate of the Petroleum Institute in Bucharest, and is Professor of Petroleum Chemistry at the Petrochemical Institute of the Polytechnical University of Barcelona. He is member-secretary of the Executive Commission of the X International Symposium on Chromatography (Barcelona 1974), and was awarded the first Osborne Prize for the Defense of Nature for his study on the chemical pollution of the Spanish Mediterranean coast, which deals with pollutants, such as petroleum, as well as other organic compounds, that are difficult to degrade.)

This article is an analysis and identification of pollutants in Spanish coastal areas, as well as of the characteristics of the residues of the principal crude and refined products.

Pollution of the sea by petroleum is, up to a certain point, a logical consequence of the role petroleum plays in technological development and in the configuration of modern life in general. Nevertheless, the volume of petroleum products spilled into the sea up to this point has reached such proportions that there is serious cause for concern from the point of view of preservation of the environment. While it is not the intent of this paper to analyze the effects of such spills, what must

* Barcelona Organic Chemistry Institute ("Juan de la Cierva" Foundation for Scientific and Technical Research).

be pointed out is that the areas suffering the most damage are the coastal areas, the very ones that comprise the framework within which many human activities (economic, recreational, etc.) are carried on. Given today's situation, therefore, merely a better understanding of the symptoms, and of the etiology, of the ecological disturbance produced by this type of pollution is not enough. We must adopt those measures that will enable us to bring about real improvement in the environment.

There can be no doubt that any efforts directed at rapid, sure identification of the origin of a pollutant will help materially in preventing spills, accidental or deliberate, and will facilitate designation of responsibility. Laws enacted by governments to cope with the problem will be effective only if the necessary analytical procedures are available to identify beyond doubt the origin of a spill, despite the fact that the penalty for such action is complicated by the different interests that may be involved, as witness the fact that only three tankers that polluted the coasts of the United States in 1966, could be penalized (31 were recognized) [1].

This paper will discuss certain aspects of the activity engaged in by the Barcelona Organic Chemistry Institute in order to identify hydrocarbon types of pollutants along Spanish coasts.

Causes of the Presence of Hydrocarbons in the Sea

Petroleum is not the only source of hydrocarbons in the sea. Recent studies have made it clear that biogenetic hydrocarbons exist in the form of plankton species, plant [2] and animal [3], and that these hydrocarbons, because they are relatively stable, can be transferred to and accumulated in

the upper trophic layers of the biosphere. However, in all cases it generally is a matter of simple mixtures, with n- and isoparaffins and olefines predominant. Hydrocarbon mixtures of fossil origin on the other hand are much more complex, qualitatively and quantitatively. Moreover, while petroleum is a natural product, it is totally foreign to the marine environment, so its presence in that environment must always be considered accidental and polluting.

Actually, petroleum spills into the sea have always been with us. Bear in mind that many petroleum deposits are known to lie beneath the continental shelf, so that a fault in the shelf's impermeable cover can allow the content to escape freely. This was the case off the coast of Southern California, when between 10 and 15 tons of crude petroleum began to escape into the Pacific Ocean every day [4]. However, since the beginning of this century, and as a consequence of the massive consumption of petroleum products, the majority of the spills that have occurred can be traced to human activities, voluntary or involuntary, and in particular to those related to the transportation and production of crude oil.

The maritime transportation concept has undergone profound changes since 1861, when the Elizabeth Watts crossed the Atlantic carrying 900 barrels of crude oil. Today, over half of the oil consumed throughout the world is carried by sea, increasing substantially the risk of polluting disasters (collisions, fire, and others). Moreover, there is the aggravating factor that a large part of this trade is handled by big tankers sailing well-defined routes (Figure 1)[5]. The most serious accident thus far, at least within this context, involved the Torrey Canyon (100,000 tons), which ran aground with a load of Kuwait crude oil off the British coast in March, 1967.

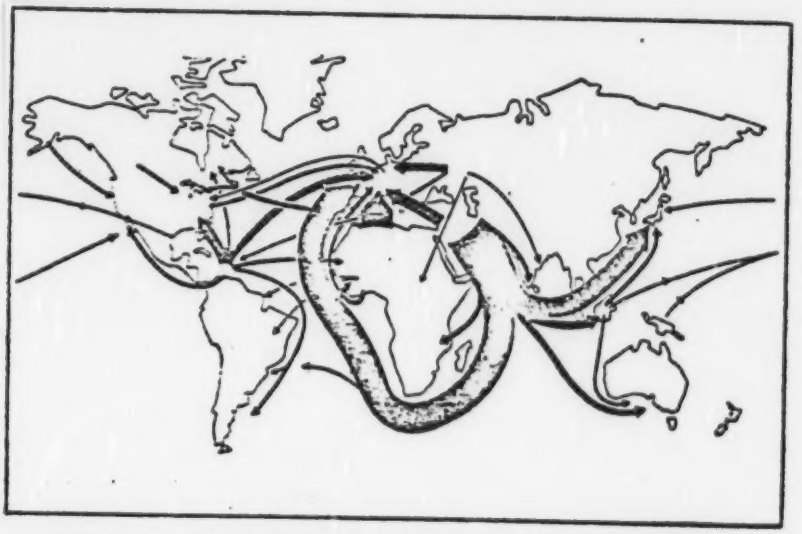

Figure 1. Maritime transportation of crude oil in 1970 [5].

But there are other types of accidents as well. Consider those that take place when tankers are loading, or unloading, particularly at mooring buoys, or between ships, when transfer lines can break, human error creeps in, and the like. True, such spills are relatively inconsequential (they rarely involve more than 5 tons of product), but they still are hard to clean up because they generally occur in quiet waters (in ports, estuaries, and the like).

The major cause of deliberate pollution in this field can be traced to washing, or deballasting, cargo tanks of tankers. Some 0.4 percent of the cargo remains as residue in the tanks, and when these latter are filled with water these residues surface and find their way into the sea unless some way is found to pump them out. The "load-on-top" technique has drastically reduced this cause of pollution, but unfortunately the technique is not yet used by many operators.

Offshore production, which should account for about 40 percent of world production by 1980, is another possible source of marine pollution, and generally is associated with cases where repairs are difficult to make. The unfortunate accident at the Union Oil Company's platform A-21, in Santa Barbara Channel, California, in 1969, is a case in point. It took three months to plug the leak, and during that time over 10,000 tons of crude oil escaped into the sea. Even a year later there was a daily loss of 9,000 liters [6]. It is to be hoped that technological advances already made in this field will make such occurrences rare.

Finally, what must be remembered is that pollution also is the result of the runoff of untreated automotive waste products (oils, lubricants, and the like), and of the fallout of hydrocarbons emitted by industrial and domestic furnaces, which can release into the atmosphere 1 or 2 percent of the fuel used in the unburned state.

It is difficult, if not impossible to make a quantitative evaluation of pollution of the seas. Estimates vary from 5 to 10 million tons per year [7], but one thing is certain, and that is that the levels of pollution are substantial (oceanographic expeditions studying the problem by gathering the neuston have found surface concentrations of 0.5 ml of oil per square meter) [8]. The harmful effects of such pollution on the environment (to the flora and fauna), and on man (social and economic activities), have been well demonstrated [9].

The types of such pollutant most often encountered, so far as their nature is concerned are:

(a) in coastal areas: fuel oils, tank washings, and crude oil;

(b) in ports: any type, but principally marine fuel oil;

(c) sewage: refined or distilled products.

Pinpointing the origin of pollutants is a complicated task, made so by the tremendous assortment of crude oil on the market, and by the changes that atmospheric agents bring about in composition. Add to this the possibility that the pollutant is a mixture of products from different sources, as often is the case with fuel oils, tank residues, refined products, and the like. At any rate, any serious attempt at identification should start with previously known features of those products that could be the source of the pollution, based on detailed knowledge of the transformations that they undergo in the environment.

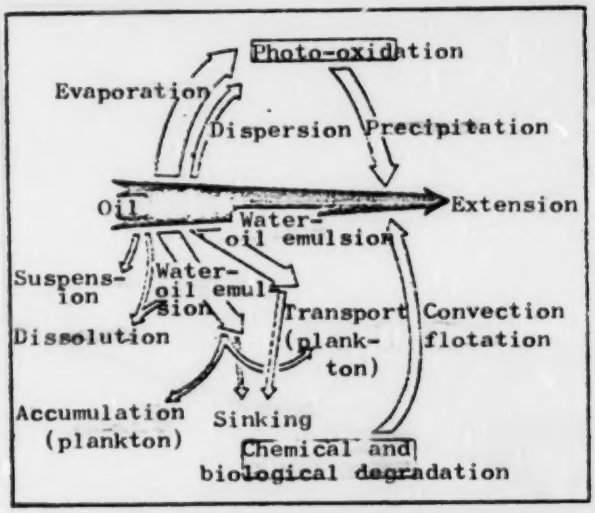

Figure 2. Petroleum aging processes in the sea.

Petroleum Behavior in the Sea

Petroleum, upon leaking or spilling into the sea, is subjected to a series of very diverse processes (Figure 2) [10] that distribute the product in the environment, and, at the same time cause it to age, or gradual convert and thus change its physical and chemical natures.

The first process after the spill is that of the extension of the product over the surface in the form of a thinning film that could, theoretically, become monomolecular. The film thickness is 0.02-0.03 mm for the first 24 hours after the spill, representing a surface concentration of the order of 20-25 tons per km^2. Later on, when the film thickness is 10^{-4} mm (80 to 90 liters/km^2), it no longer is visible to the naked eye [11].

The rate of change in this process, and its scope, depend progressively on the density, surface tension, and viscosity of the spilled product, properties that, at the same time, are undergoing constant change because of the simultaneous evaporation and dissolution of the lightest fractions. The final result is a progressive relaxation of the process lasting for 5 or 6 days, depending on the size of the spill. However, so far as the extension and mechanical transport of the spilled product is concerned, and ultimately so far as the coastal or littoral pollution is concerned, it is the action of wind and sea that is of major importance. In general, the "slick" moves with the wind at 3-4 percent of the wind speed. This favors the formation of emulsions that will, in addition, depend on the asphaltene content in the product [12]. This phenomenon became apparent in the vast extension of the spill that occurred as a result of the Torrey Canyon disaster, since known as "chocolate mousse," that can contain as much as 50 percent water and remain stable for months [9].

The processes deserving of the greatest attention, so far as identification of pollutants is concerned, are those that in some way contribute to modification of the physicochemical properties of the pollutants. Such processes can be physical, chemical, and biological as to type.

Physical processes. The principal processes of concern are evaporation and dissolution. They are involved at the quantitative level of pollution, primarily, reducing the level and, at the same time, producing products that, in time, sink into the sea as they become more dense and viscous. This is, in a general way, the origin of the "tar balls" often found on the beaches.

Evaporation of volatile fractions depends on the time that has elapsed since the spill occurred, and on weather conditions. While still substantial after several months, evaporation is most intense during the first weeks after the spill. Artificial aging tests of crude oils revealed that after 15 days of exposure residues correspond, approximately, to fractions with boiling points higher than 280°C (Table 1), and for the majority of Middle East crudes this represents a loss of approximately 50 percent of the original product.

TABLE 1

Crude	% residue	
	280° cut	Aging
Castellon	55	52.1
Es-Sider	58	59.1
Arabia light	60	59.3
Kuwait	64	65.1
Arposta	81	81.1
Boscan	93	92.2

Evaporation is enhanced by the wind and intensified during, or in areas, of strong insolation, but in general is not applicable to those fractions with boiling points above 350°C.

Nevertheless, as we shall see from what follows, changes that do occur in processes other than evaporation are of lesser importance. In

fact, the properties of the products collected after moderate aging correlate well with those found for the corresponding residues after the distillation of the original products.

Dissolution produces changes similar to those attributable to evaporation, but to a lesser extent. The logarithm of solubility in water within the same homologous series is a linear function of the molar volume of the hydrocarbon, and varies from 100 ppm for hexane to 0.001 ppm for hexadecane. Moreover, in the case of the hydrocarbons with equal numbers of atoms of carbon the increase in the solubility follows the order n-paraffins, iso-paraffins, naphthenes, and aromatics. So the elimination of a crude by dissolution can be significant as a maximum to the kerosene fractions [13]. But if the seas are heavy there will be fine dispersions, about 1 ppm of oil, representing the incorporation in the medium of one ton of product per square meter of surface per meter of depth. In any case, the stability of these suspensions depends in large measure on the medium's ionic concentration, and this latter can change in coastal areas where water flows of terrestrial origin are present.

Both phenomena (dissolution and dispersion) have been used to calculate that about 5 percent of the crude can be incorporated in the medium for depths of up to 5 meters during the first day of a spill [9].

Chemical and biological processes. The average life of a hydrocarbon, according to Calvin [14], would be greater than the presumed age of the earth (4.5×10^9 years), if the marine environment was completely abiotic and reducing (absence of oxygen). Unfortunately, at least so far as pollution problems are concerned, these conditions do not prevail in the sea. Any petroleum product spilled into the sea is subjected to chemical and biological degradation. While the process is slower than the physical one pointed out,

the effect on the different terms in the homologous series is the same.

The nature of the chemical degradation process is not known precisely, but would appear to be the result of the photooxidation of hydrecarbons of the paraffin type, with the general result compounds more soluble in water than the original ones. This process is seen as being catalyzed by the metal complexes in the residual fractions, and inhibited by the sulfur compounds, all of which concords with the fact that paraffin-base, low sulfur crudes are less affected. According to Parker [13], a maximum of 2 tons of hydrocarbons per square kilometer per day can be affected by this process under normal illumination conditions.

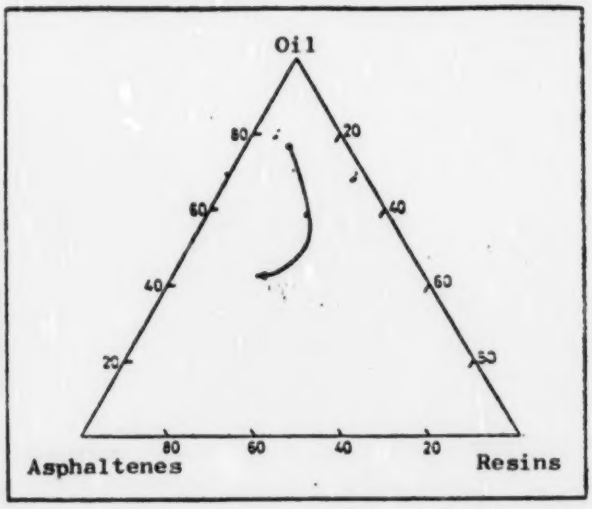

Figure 3. Variation in the composition of a crude oil with aging.

In any case, perhaps the most notable effect of photochemical change in a product is the increase in the resin and asphaltene contents [15] (Figure 3). It would appear that aromatic hydrocarbons of medium and high molecular weight have a basic part in this process. This increase is most noticeable in the case of products that had been subjected to heating (as

in the case of fuel oils, and the like) (Table 2), possibly because of the presence of olefinic fuels.

TABLE 2. % Asphaltenes

	Crude	Residues 343°C	
		Crude	Aged
Castellon	0.8	2.0	5.8
Arabia light	1.0	2.3	5.8
Es-Sider	1.9	4.2	10.2
Fuel oil	3.5	4.2	13.6
Kuwait	3.8	6.8	12.2
Amposta	13.5	19.6	34.1
Boscan	18.6	22.5	40.7

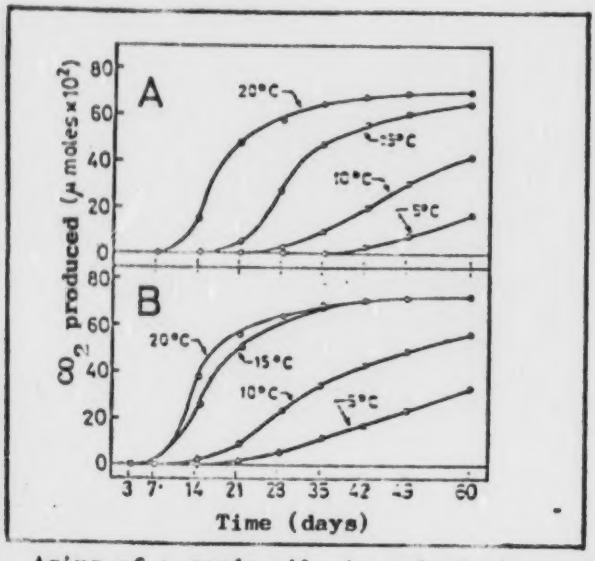

Figure 4. Aging of a crude oil, A, and of its residue, B, (70%) at different temperatures.

So far as the biological processes are concerned, over 90 species of microorganisms (bacteria and fungi) capable of subsisting in petroleum, and therefore capable of degrading it by biological oxidation, have been identified [15]. The extent of such degradation in the sea is extraordinarily dependent on water temperature, and on the presence of certain volatile fractions (naphtha and kerosene) in the spill, some components of which are bactericidal, or bacteriostatic (Figure 4) [16]. The heavy

fractions (oil, fuel oils, and the like)therefore are more biodegradable than are the crudes from which they originate, although this will not actually become apparent until several months have the spill has occurred. This degradation does not operate with equal effect on the different hydrocarbon families, but increases in the order aromatics, naphthenes, iso-, and n-paraffins.

Despite the complexity of the processes involved in the aging of a petroleum product in the sea, several parameters of its chemical composition remain stable for a long time, and undergo no change until the degradation process is well advanced. There parameters are a big help in identifying the origin of the pollutant, and we shall attempt to spell them out in what follows.

Identification of Pollutants in Spanish Littoral Regions

The initiation of studies related to the pollution of the Spanish littoral was justified by the geographic location of the country within the framework of martime transportation of crude oil, as reflected quite obviously in Figure 1, as well as by the intensive "offshore" prospecting in the area, and the coming into production of the Amposta field, the first discovery on the Spanish continental shelf.

This latter fact is perhaps what has increased public sensitivity to the problem of oil pollution, particularly along the central part of the Mediterranean coast, the economic development of which depends in large part on tourism and fishing. We therefore proceeded to determine the characteristics of Amposta-marine and Castellon crudes, from the standpoint of marine pollution, and to establish certain chemical criteria that would permit distinguishing them from other petroleum pollutants, for purposes of which we tentatively selected certain crudes (Boscan, Es-Sider, Arabia light,

and Kuwait), and a heavy type commercial fuel oil. Our purpose was to develop and perfect an analytical procedure for identifying our petroleum residues, those from the prospecting and production operations in the Ebro delta area. Products were subjected to artificial aging in containers full of sea water for 15 days while being aerated and irradiated by solar light (eight hours a day) in order to arrive at a clear understanding of the influence of environmental agents on the chemical nature of these products, and thus have available more data for use in making precise comparisons with real pollution specimens. Residues of the distillation of the original products were treated in the same way and were analyzed in order to discover any variations resulting from the simple evaporation of the volatile fractions. Residues of distillation up to 343°C were compared in both cases. This temperature was used because it is high enough to prevent chemical and biological degradation processes from having any significant effect on the properties of the residues.

When the problem of the preferred analytical method to use to characterize these products arose we found more than enough information on which to base a choice. In fact, as Adlard pointed out in a recent review, we are confronted with "an embarrassment of riches" [17].

But in practise there are few methods that combine Blumer's [18] basic conditions for unequivocal identification of the pollutant. These are:

(a) ability to differentiate products of different origins;

(b) selected differentiating characteristics that will apply for some period of time, regardless of environmental conditions;

(c) ability to distinguish between pollution specimens and biogenic hydrocarbons preexisting in the environment.

Moreover, none of the methods described to date have been shown to be so conclusive that they invalidate all the others.

The current situation then is one of selecting those characteristics that are least sensitive to the aging process, yet will provide a typical "fingerprint" of each product as quickly as possible, and from as small a specimen as possible.

We tried to combine standardized tests within the reach of any control laboratory with modern techniques of instrumental analysis. And as will be seen, they were found to yield the best information.

Table 3 lists the results of the analysis of each specimen. As may be seen, density, sulfur, nitrogen, and solid paraffin, as well as nickel and vanadium, increase as the volatile fractions evaporate. These components must be compared with the results obtained after analysis of aged products in order to make an adequate evaluation.

Generally speaking, variations in the characteristics outlined attributable to chemical and biological aging of the specimens are minimal, and show the same tendencies found by Brunnock et al [19], who analyzed Kuwait crude after the Torrey Canyon accident, that is, an increase in density as a result of the formation of asphaltic products (Table 2), and a slight decrease in the percentages of sulfur and nitrogen, the result of degradation. These characteristics can be used to fix the first bounds of the possible origin of a pollutant, within moderate aging limits. At the same time, the sulfur/nitrogen ratio is an interesting piece of complementary information.

The vanadium/nickel ratio is not affected by the aging process, practically speaking, nor are the individual values of the elements, something that is not so for those elements already mentioned, so determination of

TABLE 3. Characteristics of Crude Oils and Fuel Oil and of the Residues (> 343°C) of the Corresponding Crude and Artificially Aged Products

Crude	Arabia light	Kuwait	Es-Sider	Castellón C-1	Amposta B-1	Boscán	Fuel-oil commercial
Density, 60/60°F (ASTM D 70-70)	0,8588	0,8720	0,8434	0,8332	0,9553	1,0007	0,9471
Gravity, API	33,3	30,8	36,3	38,3	16,6	9,9	—
Sulfur, % (ASTM D 1551-68)	1,76	2,85	0,52	0,25	5,82	5,62	2,75
Nitrogen, % (Kjeldahl)	0,08	0,15	0,16	0,05	0,18	0,78	0,26
Solid paraffin, % (Shell)	3,8	4,2	7,6	11,8	8,0	2,1	8,8
Vanadium, ppm (ASTM D 2788-69)	2	28	3	<1	15	1247	37
Nickel, ppm	12	8	8,5	<1	12	160	16
V/Ni ratio	0,2	3,5	0,4	—	1,3	7,8	2,3
Sulfur/Nitrogen ratio	22,0	19,0	3,3	5,0	32,3	7,2	10,6
Residue > 343°C (ex crude)							
Density, 25/25°C	0,9456	0,9631	0,9244	0,8989	1,0067	1,0223	0,9549
Sulfur, %	2,92	4,29	0,83	0,38	7,03	6,61	3,19
Nitrogen, %	0,17	0,29	0,28	0,10	0,28	0,84	0,28
Solid paraffin, %	9,2	8,1	16,9	26,6	11,4	2,6	8,7
Vanadium, ppm	3	54	7	<1	21	1473	42
Nickel, ppm	21	12	18	<1	16	193	19
V/Ni ratio	0,1	4,5	0,4	—	1,3	7,6	2,2
Sulfur/Nitrogen ratio	17,2	14,8	3,0	3,8	25,1	7,9	11,4
Sulfur/Solid paraffin ratio	0,31	0,53	0,049	0,014	0,61	2,54	0,37
Residue > 343°C (ex crude, aged)							
Density, 25/25°C	0,9569	0,9658	0,9259	0,9002	1,0079	1,0258	0,9687
Sulfur, %	2,73	3,98	0,78	0,35	6,87	6,34	3,03
Nitrogen, %	0,14	0,22	0,27	0,10	0,27	0,76	0,28
Solid paraffin, % (test)	9,8	8,8	15,6	24,8	12,8	3,4	7,2
Vanadium, ppm	3	56	7	<1	20	1502	40
Nickel, ppm	19	12	16	<1	15,5	202	18
V/Ni ratio	0,2	4,7	0,4	—	1,3	7,4	2,2
Sulfur/Nitrogen ratio	19,5	18,1	2,9	3,5	25,4	8,3	10,8
Sulfur/Solid paraffin ratio	0,28	0,45	0,050	0,015	0,54	1,86	0,42

of these latter is very useful in identifying pollutants. Note the low metal content for Amposta-marine crude, as compared to its high sulfur content.

The table also lists solid paraffin content, an index of particular interest for the characterization of Amposta and Castellon crudes. This is true for the former because of its high sulfur ratio, and for the latter because of its absolute value. While the latter could, standing alone, introduce an error in the case of tank residue (paraffinicity), chromatography and spectrometry of specimens will result in a clear differentiation, as will be seen from what follows.

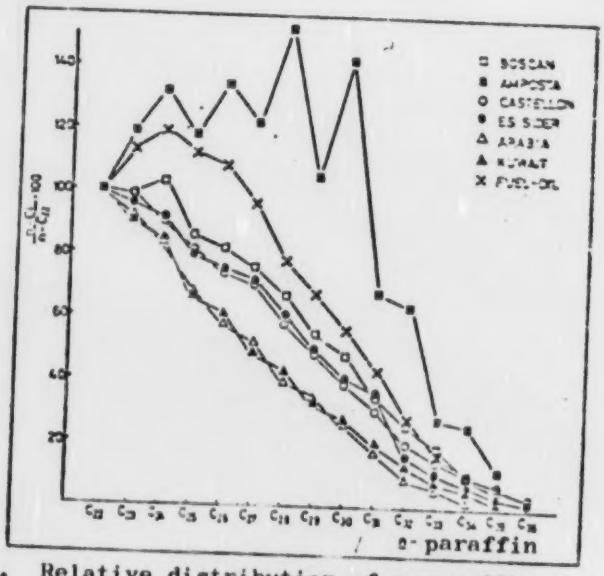

Figure 5. Relative distribution of n-paraffins in different petroleum residues (> 34°C).

Brunnock, cited above, also proposed the individual distribution of the n-paraffins, isolated by 5 Å molecular sieves, as a differential characteristic, for use in addition to the solid paraffin percentage. Figure 5 is the distribution of the products studied for this paper. As may be seen, the results are highly interesting, so far as characterization of the Amposta-

marine crude is concerned, because the distribution in the C_{22}-C_{30} region is so unusual (predominance of paraffins with carbon atoms as shown, CPI = 0.71) that there is no question of the identification of the product.

We should point out, in passing, that determination of the latter is a time-consuming process, and reproducible results are difficult to obtain, generally speaking. Furthermore, progressive biodegradation of the product causes the characteristic to lose its value. After all, almost the same data can be obtained by making chromatograms of specimens.

As a matter of fact, Ransdale and Wilkinson [20] found it possible to differentiate between the principal types of pollutants, crude, fuel oil, tank residue, that can be present by using low resolution gas chromatography (packed columns), and thus establish whether the specimens were distilled fractions, residues, or mixtures. They thus were able to compare specimens, and to perform other analyses, all with a minimum quantity of specimen, and relatively quickly.

The potential of the technique, and interest in its use in this field, have been enhanced by the introduction of the best instruments available (high-efficiency columns, selective detectors, stationary phases with high thermal stability, and others). Thus, the use of capillary columns has revealed the homologous series of isoprenoid hydrocarbons to be of particular interest because of their resistance to biological degradation (*, Figure 6) [21], (Figure 9).

Their distribution, and particularly the phytane/pristane ratio, is a new differential characteristic that must be taken into consideration [18] (Table 4) in particular when comparing or relating the different specimens (Figures 9, 10). Doing so showed up differences between Castellon

and Es-Sider crudes (Figure 6), that were, for all practical purposes, indistinguishable when low resolution gas chromatography was used (Figure 7).

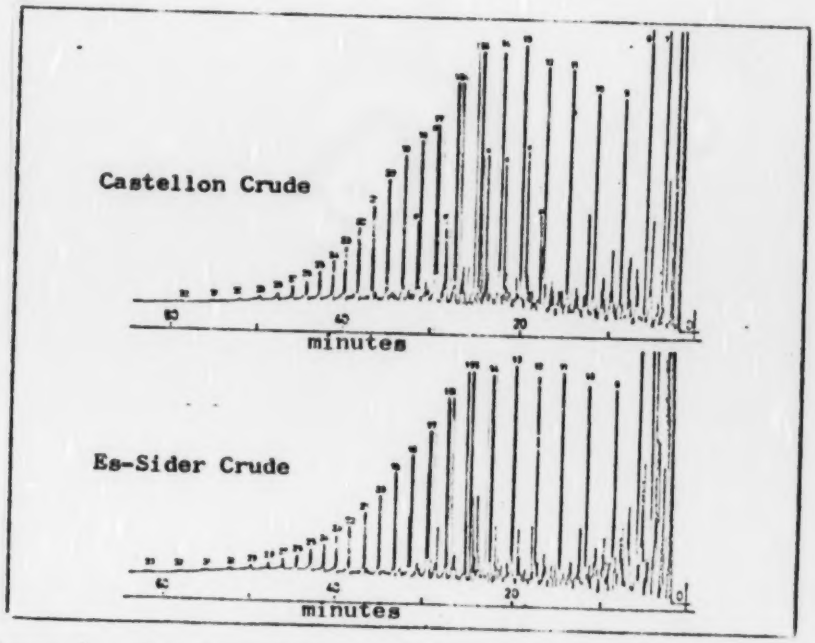

Figure 6. Gas chromatograms of Castellon and Es-Sider crudes (OV-101 capillary column; flame-ionization detector).

TABLE 4

Crude	Phytane/Pristane
Boscan	0.53
Amposta	0.60
Kuwait	0.61
Arabia light	0.70
Tia-Juana	0.94
Es-Sider	1.13
Lagunillas	1.54
Castellon	1.92

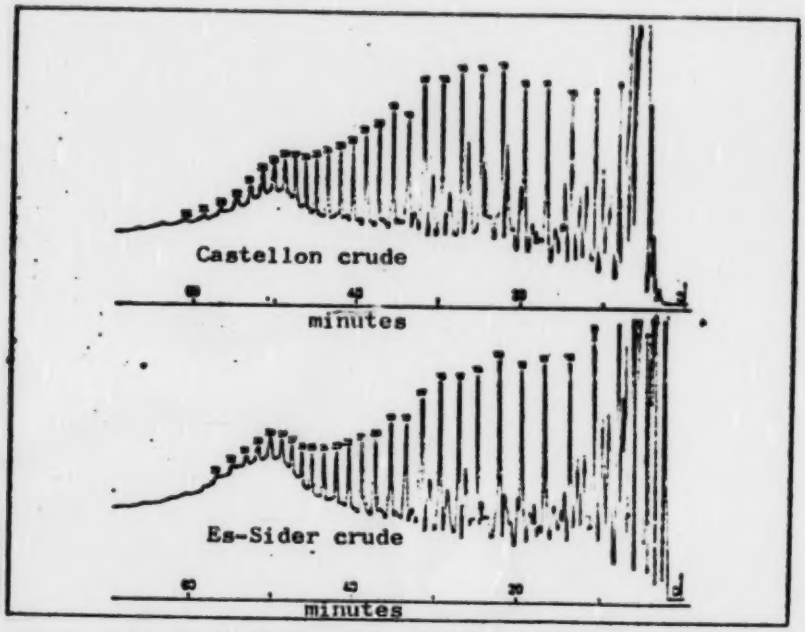

Figure 7. Gas chromatograms of Castellon and Es-Sider crudes (OV-101 packed column; flame-ionization detector).

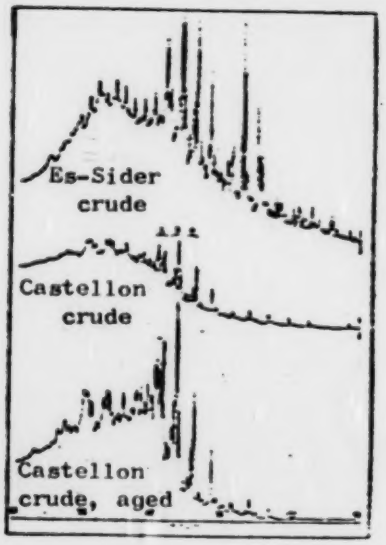

Figure 8. Gas chromatograms of Castellon and Es-Sider crudes (OV-101 capillary column; flame-photometric detector).

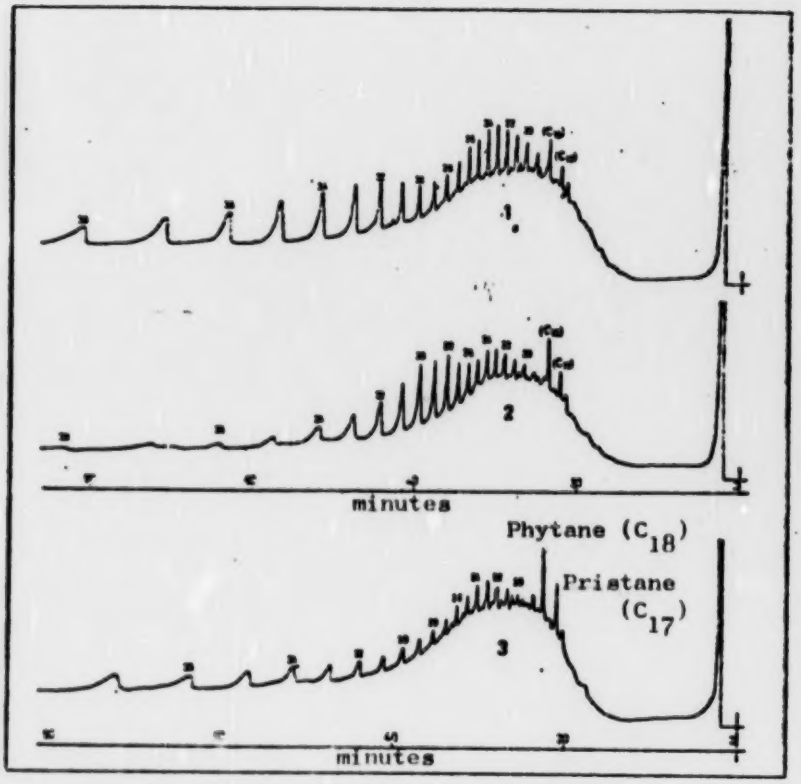

Figure 9. Gas chromatograms of three paraffinic residues (similar pristane and phytane ratios) and different degree of aging.

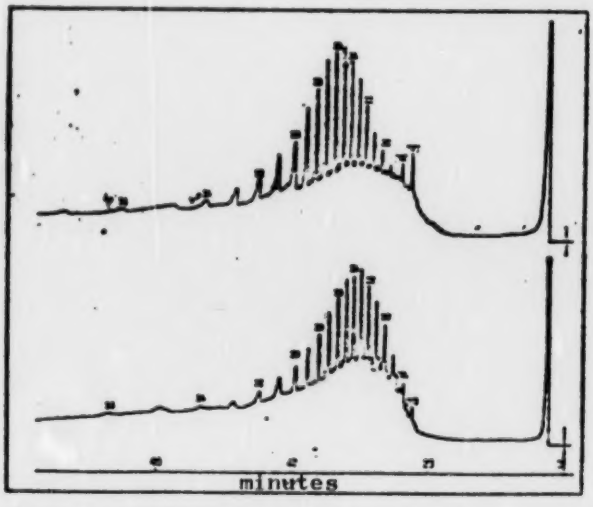

Figure 10. Gas chromatograms of two pollution specimens (different pristane and phytane ratios).

The auxiliary use of a flame-photometric detector (FPD) sensitive to sulfur compounds recently proposed by Adlard et al [2], also has been used in this case, and a complete differentiation between the two crudes was obtained (Figure 8).

TABLE 5

	Solid paraffin	
	% P	MP
Castellon crude residue	24.8	55°C
Paraffinic residue, Figure 9 (1)	29.4	72°C
Paraffinic residue, Figure 9 (3)	22.6	75°C

As has been pointed out, Castellon crude residues and the residues from cargo tanks can have similar solid paraffin contents (Table 5), although tank residues usually have a higher melting point. The two can be distinguished from each other by gas chromatography, however, because the latter show significant peaks for n-paraffins with more than 26-28 carbon atoms (Figure 9).

The distribution of the n-paraffins in Amposta-marine crude will show up on chromatograms of the crude (Figure 11), so it is unnecessary to perform a complete isolation and analysis of this crude.

There is no need to determine solid paraffin percentages if, where applicable, high-resolution gas chromatography is used, and this can be seen in Figure 12, which correlates well with the heights of the peaks for 20 to 26 carbon atom n-paraffins in the products studied.

There is, therefore, little need to emphasize the fact that high-resolution gas chromatography is a valuable aid in identifying petroleum type pollutants, combining as it does the advantages of rapid analysis and need for a minimum quantity of the specimen for the test.

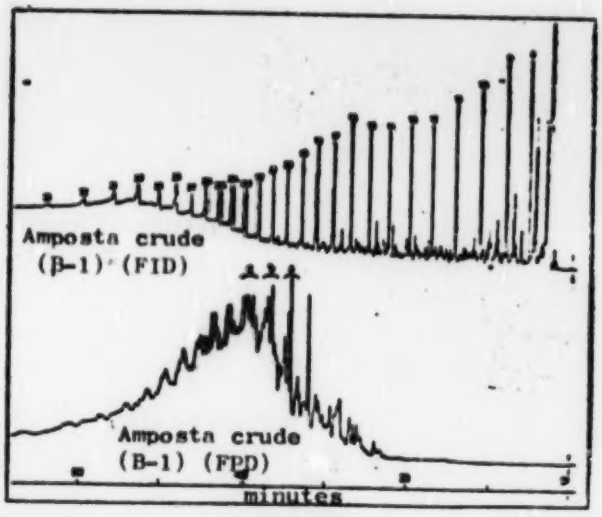

Figure 11. Gas chromatograms of Amposta-marine crude (OV-101 capillary column).

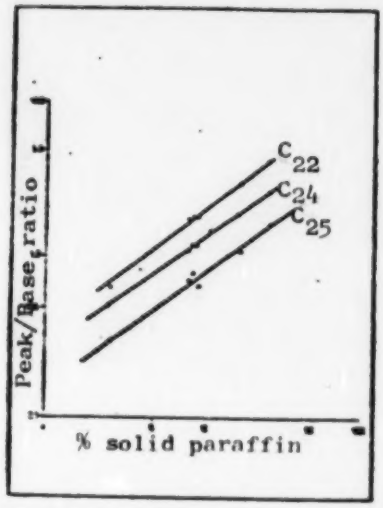

Figure 12. Solid paraffin remaining in the residues (>343°C) as indicated in Table 3 as a function of chromatographic data (the peak/base = height of the peak corresponding to the n-paraffin/ distance of the base of the peak to the chromatogram zero line).

Spectroscopic techniques, so useful in identifying and establishing the structure of organic compounds, are not as useful in this field,

but still can provide useful information. Specifically, IR spectroscopy can tell us whether we are in fact dealing with a petroleum type pollutant (it is not at all unusual to have specimens that look like tar turn out to be something other than hydrocarbon in nature). Moreover, according to Kawahara [23] it is possible to distinguish between asphalts and fuel oils by observing absorptions at 1375, 810, and 720 cm^{-1}. Our experience however is that the technique is best suited to characterize paraffinic residues (Figures 13, 14), and that in other cases the dispersion in the results is too great to be helpful.

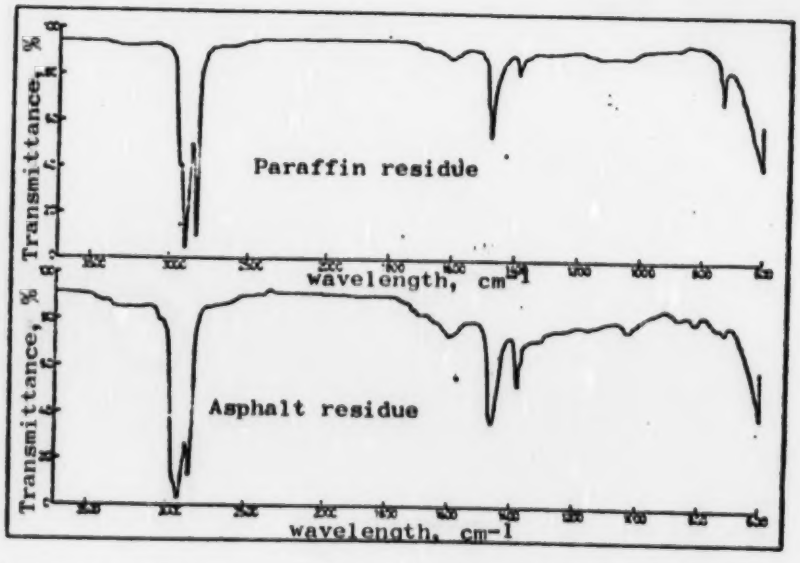

Figure 13. IR spectra for two types of pollution residues.

Generally speaking, therefore, it would be advisable to make a chromatographic (GC) and a spectroscopic (IR) examination of pollution specimens before proceeding to make a detailed chemical analysis of the specimens, particularly when the products have not had a chance

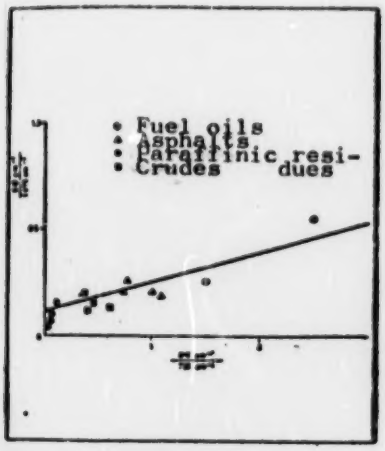

Figure 14. Absorption ratios in the IR for different types of products.

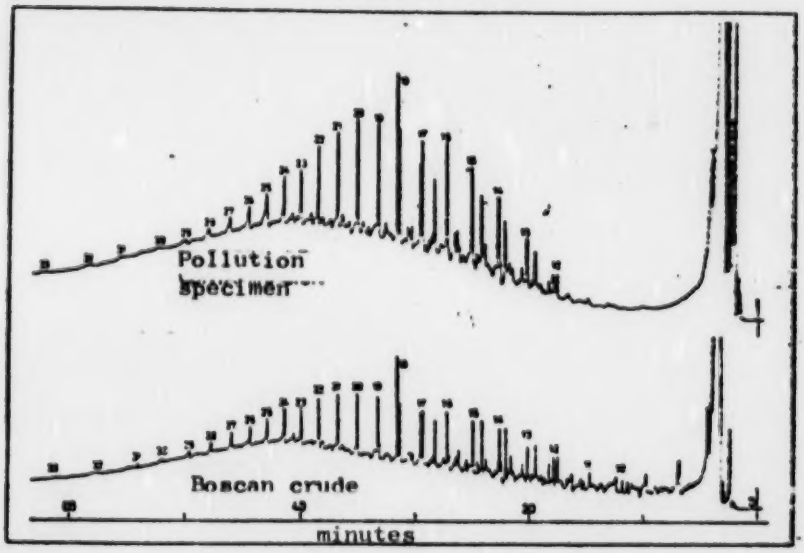

Figure 15. Identification of a pollutant.

degrade, or when we already have some idea as to possible origin.

There are many cases when basic data are available, so these determinations will be sufficient to identify a pollutant (Figure 15).

The major part of this work was sponsored by the INI/Copares-CAMPSA/Shell consortium, and we thank it for its authorization to publish the results. We also wish to thank Dr. C. R. Kolder (Shell Espana) for his interest in the development of the work, Mr. E. R. Adlard (Shell Research Limited, Thornton Research Center) for making the gas chromatograms with a sulfur detector, and ASESA, CAMPSA, ENCASO, REPESA, and Shell for providing product specimens.

BIBLIOGRAFIA

(1) T. A. Clingan: *Proc. U.S. Navel Inst.*, 95, 63 (1968).
(2) M. Blumer, R. R. Guillard y T. Chase: *Mar. Biol.*, 8, 183 (1971).
(3) M. Blumer y D. W. Thomas: *Science*, 147, 1148 (1965).
(4) A. A. Allen, S. Schlueter y G. Mikolaj: *Science*, 170, 974 (1970).
(5) *Le Pétrole*. Publicaciones de la O.C.D.E., Paris, 1973.
(6) R. W. Holmes, en: *Oil on the sea*. Plenum Press, New York, 1969.
(7) M. Blumer: *Science*, 176, 257 (1972); *The Study of Critical Environmental Problems*. MIT Press, 1971.
(8) M. H. Horn, M. Teal y H. Backus: *Science*, 168, 245 (1970).
(9) A. Nelson-Smith: *Oil Pollution and Marine Ecology*. Elek Science, Londres, 1972.
(10) FAO: *A Guide to Marine Pollution*. Gordon Pub., New York., 1972.
(11) API: *Manual on disposal of refinery wastes*. New York, 1963.
(12) C. A. Parker, M. Feegarde y C. G. Hatchard, en: *Water pollution by oil*. IP, Londres, 1971.
(13) G. D. M. McKay, A. Y. McLean, O. J. Bernancourt y B. D. Johnson: *J. Inst. Petrol.*, 59, 164 (1973).
(14) M. Calvin: *Chemical Evolution*. Oxford Univ. Press, Londres, 1969.
(15) M. Louis: *Géochimie du Pétrole*. Technip, Paris, 1967.
(16) R. M. Atlas y R. Bartha: *Can. J. Microbiol.*, 18, 1551 (1972).
(17) E. R. Adlard: *J. Inst. Petrol.*, 58, 63 (1972).
(18) M. Ehrhardt y M. Blumer: *Environ. Pollut.*, 179 (1972).
(19) J. V. Brunnock, D. F. Duckworth y G. G. Stephens: *J. Inst. Petrol.*, 54, 310 (1968).
(20) S. J. Ramsdale y R. E. Wilkinson: *J. Inst. Petrol.*, 54, 326 (1968).
(21) J. Albaigés y J. Torradas: Trabajos en curso.
(22) E. R. Adlard, L. F. Creaser y P. H. D. Matthews: *Anal. Chem.*, 44, 64 (1972).
(23) F. K. Kawahara: *Environ. Sci. Technol.*, 3, 150 (1969).

Reproduced from best available copy.